

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser



Food processing waste: Problems, current management and prospects for utilisation of the lignocellulose component through enzyme synergistic degradation



I.S. Van Dyk, R. Gama, D. Morrison, S. Swart, B.I. Pletschke*

Department of Biochemistry, Microbiology and Biotechnology, Rhodes University, PO Box 94, Grahamstown 6140, South Africa

ARTICLE INFO

Article history: Received 29 January 2013 Received in revised form 3 June 2013 Accepted 16 June 2013 Available online 5 July 2013

Keywords: Enzyme Fruit waste Lignocellulose Pectin Polysaccharide Synergy

ABSTRACT

Waste from the food processing industry (e.g., juice production) is produced in large quantities worldwide and contains high levels of lignocellulose. To some extent, value-added products are extracted from this waste, but the majority of the waste is currently unutilised and discarded. Energy generation from this waste has been investigated in the form of production of biogas, hydrogen and bioethanol. Efficient bioethanol production requires the enzymatic hydrolysis of the total polysaccharides within this waste into monomer sugars for further fermentation into ethanol. Factors limiting this process are the complexity of the lignocellulose, its recalcitrance and insolubility and the number of enzymes required to degrade it. Obtaining complete enzymatic hydrolysis of these substrates requires an understanding of the composition of the polysaccharides and their associations within the overall substrate. This will allow appropriate selection of enzymes. It has also been established from work on other lignocellulose substrates that the associations between polysaccharides pose an obstacle to their hydrolysis and cooperative enzyme interaction is required to overcome these obstacles. With respect to the enzymatic hydrolysis of food waste, the knowledge gaps have been identified as: (1) accurate knowledge of the polysaccharide composition and structures; (2) knowledge about the associations that exist between different polysaccharides; (3) and the enzymes required for hydrolysis of the overall polysaccharide component and the synergistic interactions between these enzymes. This review investigates these aspects in literature, exposing the gaps in knowledge, while making proposals for future work that could assist in the utilisation of food waste, through enzyme synergistic degradation, as a potential feedstock for biofuel production.

© 2013 Elsevier Ltd. All rights reserved.

Contents

1.	Introd	luction		522		
	1.1.	Current	management of food processing waste	522		
	1.2.	Current	value-added products obtained from food waste	523		
	1.3.	Current	technologies for energy generation from food processing waste	523		
2.	Polysa	accharides	s in fruit and vegetable waste	525		
	2.1.	Compos	ition of fruit and vegetable waste	525		
	2.2.	Polysaco	charide structures in food waste	525		
		2.2.1.	The structure of pectin	526		
		2.2.2.	The structure of xyloglucan.	526		
		2.2.3.	The structure of glucuronoxylan.	526		
3.	Enzyn		onversion of polysaccharides in fruit and vegetable waste.			
	3.1.	Factors	affecting enzymatic lignocellulose bioconversion	526		
	3.2.	Enzyme	s required to degrade polysaccharides in food waste	527		
	3.3.	. Interactions and associations between polysaccharides in food waste and their impact on enzymatic bioconversion				

^{*} Corresponding author. Tel.: +27 46 603 8081; fax: +27 46 622 3984. E-mail address: B.Pletschke@ru.ac.za (B.I. Pletschke).

	3.4.	Enzyme synergism	528
	3.5.	Enzyme bioconversion or synergy studies on food waste (pectin containing substrates)	528
4.	Produ	cts from enzymatic bioconversion of fruit and vegetable waste and challenges for fermentation	529
5.	Conclu	ision and future prospects.	529
Ack	nowled	gements	529
Refe	erences	- 	529

1. Introduction

Large quantities of waste material are generated annually from agricultural activities and processing of agricultural products. This includes wastes such as corn stover, sugarcane bagasse, rice and wheat straw, many of which are currently under investigation as potential feedstocks for value-added products such as bioethanol production. However, a different category of waste from the food processing industry remains largely underutilised and should be investigated for further beneficiation. Examples of such wastes include citrus, apple and grape waste, often referred to as pomace, as well as sugar beet pulp remaining after processing of sugar beet. These wastes contain high levels of polysaccharides which could potentially also be utilised for production of bioethanol.

Food processing wastes are produced as solid and liquid wastes. The solid waste is the portion of the starting material that cannot be utilised in the production of the intended products, such as the skins, pips and fibres of fruit which are removed in the production of juice. This review will only focus on solid waste, as the polysaccharides are found mainly in this waste type. Significant volumes of solid waste are produced globally from just a few of the main food processing industries (see Table 1).

1.1. Current management of food processing waste

Solid waste from food processing is currently managed in various ways. Many factories simply dump the waste close to the plant. Since these wastes have high nutrient levels and water content and can support bacterial growth and fermentation, these may cause odours and other environmental problems [11,12]. In some cases, the waste may be transported to a landfill site for

disposal, which could lead to additional costs as some countries may charge landfill disposal fees [12]. It is estimated, for example, that \$10 million is spent annually on the disposal of apple pomace in the USA [13]. Occasionally, waste disposal may take place through incineration. However, the energy input is costly due to the low calorific value and the high water content [12]. Incineration also results in air and environmental pollution [14].

A further means of disposal of food waste is through its utilisation as animal feed, mostly for cattle feed [12]. The waste may be dried and formed into pellets prior to sale as animal feed [15,3]. However, most food wastes have low protein content and are therefore not ideal for animal feed. High lignin content in some wastes, for example olive waste and sugarcane bagasse, also limits utilisation as animal feed as it makes the waste difficult to digest [12]. Different wastes have different potentials for use as animal feed. For example, potato waste is very high in potassium and can therefore only be utilised for cattle feed as it is not suitable for other animals [12]. Where wastes are dried prior to being used as animal feed, additional costs may be incurred, which are rarely recovered from the cost of sales. The use of apple pulp, particularly, as an animal feed is limited due to its rapid spoilage unless drying can take place immediately after processing [11]. Protein content and digestibility of pomace may be enriched through growth of microorganisms (such as Pleurotus ostreatus and Candida utilis), on the pomace which makes it more suitable for animal feeding [16].

Food waste can also be utilised as a soil conditioner or fertiliser [17]. This can be done through spreading of the untreated food waste on the soil, thereby increasing the organic content and microbial biomass of the soil. Tomato waste and olive husks have been utilised in this manner. Citrus waste contains compounds

Table 1Reported quantities of fruit and vegetables produced worldwide and the waste generated as a result. Waste figures are approximate and based on literature reports of the percentage of the original fruit or vegetable that is not utilised for generating products such as juice. (MT=metric tons).

Fruit/vegetable	Total global production in 2010 [1]	Approximate waste produced in 2010	Reference
Apple	69 569 612 MT	Approximately 25–35% of the dry mass is waste – 17,392,403–24,349,364 MT	[2]
Citrus: Grapefruit	6,957,837 MT	Approximately 3,478,918 MT of Grapefruit waste	[3]
Citrus: Lemons and limes	14,244,782 MT	Approximately 4,985,673 MT to 6,410,151 MT of waste (half of the fruit)	[4]
Citrus: oranges	69,416,336 MT	Up to 70% of global production is used in the manufacture of juices, marmalades, etc. Between 50% and 60% of the fresh fruit weight are waste – 24,295,717 MT and 29,154,861 MT of waste	[3]
Sugar beet	228,452,073 MT	For every 1 t of Sugar beet processed, 70 kg of exhausted dried pulp or 250 kg of exhausted pressed pulp are produced. This equals 22,845,207 MT of dry SBP or 57,113,018 MT of pressed SBP.	[5]
Olive	20,578,186 MT	For every 100 kg of olives processed for oil, between 50 kg and 110 kg of "Black water" (runoff rich in antioxidants and protein) is produced. Approximately 20% of the olive fresh weight will be the endocarp fragments - 3,704,073 MT of olive endocarp waste.	[6,7]
Grapes	68,311,466 MT	Approximately 10,929,834 MT of grape pomace was produced (20% of grapes become pomace in winemaking)	[7]
Banana	102,114,819 MT	30–40% waste	[8], [9]
Pineapple	19,418,478 MT	40–80% waste. At 45% waste, 8,738,315 MT of waste is produced every year.	[10]
Potatoes	324,181,889 MT	Peel waste can be between 15% and 40% depending on the processing method used. This will approximate to 48,627,283 MT and 129,672,755 MT of waste generated annually.	[7]
Tomatoes	145,751,507 MT	In the processing between 3% and 7% is lost as waste. Approximately 4,372,545 MT and 10,202,605 MT of waste were generated in 2010.	[7]

with fungistatic activity and can be used in soil to protect fruits and vegetables from fungal infections. In some cases, composting can be undertaken prior to utilisation as a soil amendment, but this is a lengthy process. Composting of grape waste is extensively reviewed by Arvanitoyannis et al. [17]. Haddadin et al. [18] investigated composting of olive pomace in a bioreactor for 50 days using *Trichoderma harzianum* and *Phanerochaete chrysosporium*, with urea added as a nitrogen source.

1.2. Current value-added products obtained from food waste

Several reviews are available on the value-added products that may be obtained from various food wastes [19,12,13]. One of the most prominent products that can be obtained from food waste is pectin, which is extensively used in the food industry as a gelling agent, thickener and stabiliser in foods and is mostly extracted from apple and citrus pomace, but can also be obtained from sugar beet pulp [19]. However, the pectins from different sources display different characteristics. For example, pectin from sugar beet does not form gels, but can still be used as an emulsifier or stabilizing agent [20].

Dietary fibres can be extracted from food waste and used in various food applications. Human consumption of dietary fibre is important in the prevention of disease, such as constipation and haemorrhoids, but can also lower cholesterol and may reduce the risk of colon cancer [9,21]. Dietary fibres have been extracted from apple pomace [22], sugar beet pulp [23], grape waste [24], sweet potato [25] and banana peels [9].

Phenolic compounds are found in many fruits and vegetables and have several properties which make them useful as antioxidants, antimicrobials and anticancer compounds, as well as having cardio-vascular protective properties [26]. Phenolic compounds may differ between different sources of fruit and can be present at different concentrations. High levels of phenolics are found in red grape pomace (> $100 \,\mu\text{g/mg}$), while apples contain much lower total phenolics (< $20 \,\mu\text{g/mg}$) [27]. Some of the phenolics in grape skins are gallic acid, rutin, anthocyanin derivatives and quercetin derivatives, while apple skins contain catechins, caffeic acid, chlorogenic acid, rutin, phloridzin and quercetin derivatives [27,19].

Lycopene is a compound found in extracts of tomato skins and other red fruits, such as watermelon and guava. It is a type of carotenoid compound and has antioxidant properties and application for the decrease of cancer and cardiovascular diseases [7,28]. Grape seed oil is also a valuable commodity which can be extracted from grape seeds. Vanillin is a natural product that can be extracted from vanilla beans; however, it may also be biosynthesised from ferulic acid, a product of lignocellulose degradation [29,30]. Xylitol can be produced from xylose and used as a sweetener in the food industry [31]. Food waste has also been utilised for the production of enzymes [32–34].

A major obstacle in the production of ethanol from citrus waste is the presence of D-limonene, which can be toxic to microorganisms involved in fermentation [35]. However, D-limonene has beneficial uses and can be used as a flavour and fragrance additive in perfumes, soaps, foods, chewing gum and beverages. It has also been used to dissolve cholesterol-containing gallstones, relieve heartburn and as an anti-cancer agent [36]. As such, it can be extracted from the waste, as another value-added product, prior to fermentation.

1.3. Current technologies for energy generation from food processing waste

Food processing waste can be used for energy generation. Several non-biological technologies have been used for energy generation from food waste. These include thermochemical conversion technologies such as combustion, gasification, hydrothermal processing, liquefaction and pyrolysis [37]. The high water content of the waste will affect the effectiveness of these technologies. Recent studies have also demonstrated effective conversion of cellulose to glucose through the use of sulfonated carbon catalysts [38,39].

Biological methods for energy generation from food waste include the production of hydrogen, biogas and bioethanol. Hydrogen production can take place through many different processes. An environmentally friendly method of producing hydrogen is through biological processes involving algae, photosynthetic bacteria, cyanobacteria or anaerobic fermentation bacteria [40] which can utilise industrial and agricultural wastes as substrates [41].

Hydrogen production through anaerobic digestion is a complex process and may involve many different bacteria and enzymatic processes. There are three main methods of hydrogen production, utilising bacteria, which have been reported in literature:

- Dark-fermentation (which does not involve light): Under anaerobic conditions, hydrogen is produced as a by-product during acidogenesis. However, the yield is low and the rate is slow [42].
- Photo-fermentation (which requires light as the source of energy):
 Photo-heterotrophic bacteria can utilise organic acids such as acetic, lactic, and butyric acids, produced during acidogenesis, to produce hydrogen [42]. Oh and co-workers reported a hydrogen yield of 2.8 mol/mol substrate with Rhodopseudomonas palustris and acetic acid [43].
- Combined-fermentation (dark and photo-fermentation combined): This may involve sequential or simultaneous combination of dark and photo-fermentation processes. Yokoi et al. [44] performed sequential dark-photofermentation with *Clostridium butytricum*. Enterobacter aerogens and Rhodobacter sp. M-19, on sweet potato starch residue and reported a hydrogen yield of 7.0 mol/mol glucose. Yokoi et al. [45] also reported a high hydrogen yield of 6.6 mol/mol glucose by combined dark-photofermentation of starch using C. butyricum and Rhodobacter sp. M-19. Hydrogen production rates are dependent on light intensity, carbon source and microbial culture [42], but it would appear that the combined fermentation approach seems to be more appealing, as the process results in increased hydrogen yields. However, the disadvantage of this approach is that, due to differences in organic acid production and consumption rates, organic acids may accumulate which results in decreased light penetration because of suspended solids [42].

Feng et al. [46] investigated the production of bio-hydrogen from apple pomace, combined with river sludge, in the presence of anaerobic bacteria. They were able to produce sustainable quantities of bio-hydrogen, as well as other useful by-products such as acetic acid, ethanol and butyric acid [46]. Acetic acid may then be used to produce methane by the action of methanogenic bacteria [42].

Biogas consists mostly of methane (50–70%) and can be used to supply energy for lights, cooking, water pumps and electric generators [47] The production of biogas from lignocellulosic waste is an anaerobic process. Under anaerobic conditions, biogas and organic fertilizer can be produced from organic wastes by the action of various microorganisms [47]. Some advantages of producing biogas through anaerobic digestion, compared to other waste treatment strategies, include increased effectiveness in pathogen removal, reduced production of biomass sludge compared to aerobic treatment methods and decreased odour emissions [47]. Several studies have used food waste for the production of biogas. Cuzin et al. [48] used cassava peel and produced 0.217 m³ of biogas, Kalia et al. [49] used apple pomace (0.270 m³), Somayaji

 Table 2

 Polysaccharide compositions of different sources of fruit or vegetable waste.

Source	Polysaccharide composition (sugars)	Comment	Reference
Apple	Fucose, rhamnose, arabinose, galactose, glucose, xylose, mannose, galacturonic acid Glucose (22.7%), fructose (23.6%), sucrose (1.8%), xylose (0.06%), pectin (3.9%) Xylose and fucose part of fucogalactoxyloglucan, the main emicelluloses of apple cell wall	Apple skins: Phenolics, anthocyanins Pomace: Phenolics (0.99%)	[27] [11] [62]
	Rhamnose, arabinose, xylose, mannose, galactose, glucose, galacturonic acid	Skin, flesh and pith characterised separately Proteins and lipids (highest in epidermis)	[63]
	Lignin (23.5%), cellulose (7.2%), hemicelluloses Glucose (22.7%), fructose (23.6%), sucrose (1.8%), xylose (0.1%)	Pomace	[34]
	Pectin (11.7%), emicelluloses (24.4%), cellulose (43.6%), lignin (20.4%)	Dietary fibres	[22]
itrus	25% pectin, 26% hexosans, 7% pentosans Cellulose (22%), hemicellulose (11%), lignin (2.19%) (8.1% glucose, 12% fructose, 2.8% sucrose, 25% pectin)	Citrus waste Citrus waste (orange) Protein (6%), limonene (3.78%)	[15] [35]
	Pectic polysaccharides (homogalacturonan, rhamnogalacturonan I and II, Type I arabinogalactan and arabinan) (55%) Cellulose (22%), xyloglucans (10%), heteromannan (2%), heteroxylan (2%)	Albedo tissue from oranges	[64]
	Pectin (15-25%), cellulose (8–10%), hemicellulose (5–7%) Pectin (14.2%), Lignin (8.9%), Cellulose (20.8%), hemicellulose (17.2%)	Citrus waste (oranges) Mandarin peel, protein (7.5%), Fat (1.6%), limonene (18.58%)	[65] [58]
	Pectin (23%), lignin (7.5%), cellulose (37.1%), hemicellulose (11%)	Orange peel, protein (9.1%), Fat (4%)	[58]
rape	Fucose, rhamnose, arabinose, galactose, glucose, xylose, mannose, galacturonic acid Neutral polysaccharides – cellulose, xyloglucan, arabinan, galactan, xylan and mannan (30%) 20% pectins	Skins Total phenolics and anthocyanins Grape pomace 15% proanthocyanidins, lignin, proteins and phenols	[27] [66]
	Neutral polysaccharides (cellulose, xyloglucan, arabinan, arabinogalactan (Type I and II), xylan, mannan); pectic polysaccharides (30–35%) Rhamnose, fucose, arabinose, xylose, mannose, galactose, glucose, uronic acids	Grape berry skins Methanol, acetic acid, proanthocyanidins	[67]
	Lignin (39.6%), cellulose (36%), hemicellulose (24%) (14.9% xylans, 3.7% arabinans, 2.0% mannans, 3.9% galactans)	Grape stalks Tannins (6%)	[68]
	Lignin (17.4%), cellulose (30.3%), hemicellulose (21%)	Grape stalks: 15.9% tannins, 6.1% protein	[69]
	Lignin (33–47%), cellulose (25–38%), hemicellulose (15%) (10% xylan, 4% araban) Cellulose, xyloglucan, pectic polysaccharides (homogalacturonan, rhamnogalacturonan I and II) Arabinogalactans I and II found in RG I	Grape stalks Grape berry cell walls	[70] [71]
	Seeds – lignin (64%), cellulose (17.75%), hemicellulose (18%), pectin (0.25%) Skins – lignin (59%), cellulose (6%), hemicellulose (31%), pectin (4%)	Grape pomace fibre (seeds and skins)	[32]
	Neutral polysaccharides (cellulose, xyloglucan, arabinan, galactan, xylan and mannan) (30%) Acidic pectic substances (20%)	Grape pomace: 15% insoluble proanthocyanidins, lignin, structural proteins and phenols	[72]
live	Seed husks – cellulose (36.4%), hemicellulose (26.8%), lignin (26%). Glucuronoxylan	Protein & fat	[73]
	main hemicelluloses Stoned – cellulose (31.9%), hemicellulose (21.9%), lignin (26.5%) Pectic polysaccharides (35% – galacturonan 12%, arabinan 20%), glucuronoxylan (11%), xyloglucan (3%), mannan (1%), cellulose (14%)	Olive pulp after processing	[74]
	Cellulose (31.9%), hemicellulose (21.9%), lignin (26.5%) Rhamnose (1–3%), arabinose (17–20%), xylose (17–20%), mannose (2%), galactose (4–5%), glucose (31–34%), uronic acids (22–23%)	Stones and husks mixed Olive pulp (stones removed). Alcohol insoluble fractions of olives at different stages of ripening Protein content 18–24%	[75] [76]
ıgar beet pulp	Values in mg/g: Rhamnose (23.1), Arabinose (181.4), xylose (14.6), mannose (12.4), galactose (45.3), glucose (199.9), uronic acid (184)	Pulp	[29]
rr	Cellulose (21.5%), hemicellulose (55%), lignin (2.2%)		[77]
	Pectin (21.1%), cellulose (27.4%), hemicellulose (28.1%), lignin (3.1%) Lignin (2%), glucose (20%), mannose (1%), galactose (4%), xylose (1%), arabinose (20%),	Protein (10.8%)	[33] [78]
	rhamnose (1%), unonic acid (18%) Rhamnose (2.4%), fucose (0.2%), arabinose (20.9), xylose (1.7%), mannose (1.1%),	Troteins (78)	
	galactose (5.1%), galacturonic acid (21.1%), glucose (21.1%) 19% pectin, 21% pectin associated arabinan, 24% cellulose Homogalacturonan,		[79] [80;81]
	rhamnogalacturonan, arabinan, glucomannan, xyloglucans (incl. Fucose) Cellulose (22–30%), hemicellulose (24–32%), pectic substances (24–32%), lignin (3–4%) Glucose (24.3%), arabinose (19%), galacturonic acid (15.3%), galactose (4%), xylose (1.4%), mannose (1.4%), rhamnose (1.2%)		[5]
alm date fibres	Lignin (49.9%), polysaccharides (20.9%) – glucan, xylan, galactan, mannan, arabinan		[82]
otato pulp	Galactose (55%), arabinose (10%), galacturonic acid (17%), rhamnose (1.4%) – no fucose, xylose or mannose Homogalacturonan and rhamnogalacturonan I	After starch removal	[83]
herry pomace	Cellulose (18.4%), hemicellulose (10.7%), pectin (1.51%), lignin (69.4%)		[22]
ack currant	Cellulose (12%), hemicellulose (25.3%), pectin (2.73%), lignin (59.3%)		[22]
ear pomace	Cellulose (34.5%), hemicellulose (18.6%), pectin (13.4%), lignin (33.5%)		[22]
irrot pomace	Cellulose (51.6%), hemicellulose (12.3%), pectin (3.88%), lignin (32.2%)		[22]
weet potato	Cellulose (31.19%), hemicellulose (11.38%), pectin (15.65%), lignin (16.85%) Glucose (56.05%), uronic acid (22.95%), galactose (10.39%), arabinose (3.68%), xylose (3.33%), rhamnose (2.05%), mannose (1.27%)	Dietary fibre. Differences between different varieties. Average values	[25]

Table 2 (continued)

Source	Polysaccharide composition (sugars)	Comment	Reference
Loquat fruit	Pectic polysaccharides form 70% of polysaccharides, xyloglucans present	Fruit	[84]
Aloe vera	High mannose, glucose and uronic acids (plus rhamnose, fucose, arabinose, xylose, galactose) Pectins and mannans. 2 types of mannose containing polysaccharides. Acemannan in the filet 60–79% carbohydrates, highest lignin in skin (19.62%)	Skins, filet and gel Proteins and lipids, dietary fibres	[85]
Prickly pear	Cellulose (27%), other polysaccharides (35%), lignin (2.4%) Uronic acid (35.6%), rhamnose (3.3%), arabinose (9.3%), xylose (4.5%), galactose (8.4%), glucose (29.3%)	Skins. Fats and oils removed. Proteins (8.6%)	[86]
Black currant and blackberries	Xyloglucan mannose dominant in black currants, xylose in bilberries		[87,88]

[50] used mango peel (0.330 m^3) , while Prema et al. [51] used a mixture of fruit and vegetable waste (0.120 m^3) .

In some cases, multiple products may be produced from one type of waste. For example, Pourbafrani and co-workers were able to produce 39.64 L of ethanol, 45 m³ methane, 8.9 L limonene and 38.8 kg pectin from one ton of citrus waste [35].

Various food wastes have been utilised for the production of bio-ethanol, including banana peels [52-54], sugar beet pulp [55], pineapple waste [10], grape pomace [55,56], potato peel waste [57] and citrus waste [58,59,35]. Due to the complex nature of the lignocellulosic component of waste, some studies utilised enzyme preparations containing cellulases and pectinases in order to degrade the complex polysaccharides to provide additional sugars for fermentation [57,10,53,59,54]. In most cases, Saccharomyces cerevisiae was utilised for fermentation, although Ban-Koffi and Han [10] also used Zymomonas mobilis and Korkie et al. [56] utilised Pichia rhodanensis. S. cerevisiae has the disadvantage in that it can only utilise hexose sugars [60], but other fermentative organisms can be used for utilisation of pentose sugars for ethanol production. Z. mobilis has proven to be a very productive ethanol producer with a tolerance for high ethanol concentrations [61]. A limitation with respect to ethanol production is the utilisation of the full polysaccharide fraction of the waste. This requires optimisation of the enzymes and their ratios required to hydrolyse the polysaccharides into monomers. Knowledge of the polysaccharides present in waste will assist in the selection of the appropriate enzymes for inclusion in an optimised enzyme cocktail.

2. Polysaccharides in fruit and vegetable waste

Fruit and vegetable waste contain significant quantities of polysaccharides. Enzymatic hydrolysis of these polysaccharides can provide monomer sugars for fermentation into ethanol. Polysaccharide composition provides an indication of the enzymes required for bioconversion. Although extensive research has been conducted on enzyme selection and optimisation for bioconversion, this was carried out on substrates such as wood and grass. However, the polysaccharides in food wastes are different from these substrates and therefore require a different approach for their bioconversion.

2.1. Composition of fruit and vegetable waste

Table 2 summarises the compositions of food waste as reported in literature with a specific focus on the polysaccharide/lignocellulose components. It should be noted that the specific composition of waste at a particular processing plant may differ from the same waste at a different plant as it may be affected by the type of processing. For example, where enzymatic extraction methods are used, some of the polysaccharides may be degraded by the

enzymes, resulting in a lower percentage of that polysaccharide in the final waste. The most common enzymes used in juice extraction are pectinases, which will reduce the pectin content in the waste. Other enzymes may include amylases, proteases, cellulases and hemicellulases (see review by Ribeiro et al. [89]). However, it should be noted that the European Union regulates the use of enzymes in juice production which limits the permissible enzymes to pectinases, proteases and amylases (EC regulation no. 1332/2008). Should only these enzymes be utilised, the cellulose and hemicellulose fractions would remain largely intact.

Current knowledge of polysaccharide composition of food waste is generally inadequate. In some cases only the dietary fibre is studied and in other cases only skin composition is studied, rather than total pomace, which would include seeds and pith content. Free sugars such as fructose and sucrose may also be included in the reported composition, which does not form part of the polysaccharide network. It is also not clear which sugars contribute to which polysaccharide, as in-depth structural analyses are not generally carried out. Thus the percentage polysaccharides, as well as the type of polysaccharides, are not well-defined for many types of wastes. This poses an obstacle in the identification of enzymes required for bioconversion of these wastes.

The least characterised polysaccharides in food waste are the hemicellulose fractions, with most studies on food waste having been performed on the pectin fraction. The hemicellulose fraction is also not consistent, as there is an indication that different hemicellulose structures may occur in different food wastes. As the hemicellulose fraction can form a significant part of the polysaccharides in fruit waste, it is important to understand its structure and how interaction with other polysaccharides takes place. Lack of knowledge in this regard could hamper the selection of enzymes for complete bioconversion of such waste.

High levels of pectin are found in all food wastes which are generally only present at very low levels in the secondary cell walls of lignocellulose substrates such as wood and grass. The chemical composition and structure of pectin and its interaction with other polysaccharides is further described in Sections 2.2.1 and 3.

What is also notable about the reported composition of food waste is the absence of common polysaccharides such as xylan, which forms a large percentage of lignocellulose substrates such as grasses or wood. While a small percentage of mannan is reported to be found in some wastes (grape and olive waste), it is not clear what the type and structure of the mannans in these substrates are and whether they resemble the common mannans found in wood and grasses.

2.2. Polysaccharide structures in food waste

One of the main polysaccharides in food waste is cellulose. As the structure of cellulose is well-characterised and consistent between different sources, it will not be further discussed in this review (see [90,91]).

2.2.1. The structure of pectin

Pectin forms an important structural component in plant cell walls. Primary cell walls of dicotyledonous plants can contain approximately 35% pectin. On the other hand, secondary cell walls in grasses contain only 2–10% pectin with wood tissues containing approximately 5% pectin [92]. In fruit and vegetables, the pectin content can be very high as can be seen in Table 3. Voragen et al. [92] provides an updated review on the structure of pectin and various models that have been proposed over the years to elucidate the structure.

Pectin is the most complex polysaccharide known in nature and contains a variety of structural features, namely homogalacturonan, rhamnogalacturonan I and rhamnogalacturonan II [92]. Homogalacturonan (HG) is the major component in pectin and can constitute up to 60% of the pectin, although the exact content of HG may differ depending on the source (see Table 3) [92]. It consists of a polymer of α-1,4-galacturonic acid residues with different degrees of methyl esterification at C-6 and/or acetylation at O-2 or O-3. The degree of methyl-esterification differs between pectins from different sources and has an impact on the gelling properties of the pectin [92]. Xylogalacturonan is a type of HG chain that has xylose substituents on the galacturonic acid backbone, while the unsubstituted galacturonic acids may still contain methyl-esterification [92]. Xylogalacturonans are mainly found in fruits and seeds, with the incidence dependent on the source (see Table 3).

Rhamnogalacturonan I (RGI) has a backbone of alternate rhamnose and galacturonic acid repeating units [\rightarrow 4)- α -p-GalA-(1 \rightarrow 2)- α -L-Rha-(1 \rightarrow]. The number of repeats of this subunit can differ between sources of RGI [92]. Neutral sugar side-chains are found as substitutions at O-4 of the rhamnose residues and consist of galactosyl and/or arabinosyl residues [92]. These substituents may be single sugars or polymers, such as arabinogalactan I and arabinan. Neutral sugar branching can form 20–80% of the RGI (see Table 3) [92]. Unsubstituted galacturonic acid residues in the backbone are acetylated at the O-2 and O-3 positions [92].

Rhamnogalacturonan II (RGII) is a unique structural feature of pectin and can contain a large number of unusual monomers with a large number of linkages. The backbone consists of galacturonic acid repeats, with side chains consisting of apiose, aceric acid, 3-deoxy-lyxo-2-heptulosaric acid and 3-deoxy-manno-2-octulosonic acid [92]. The structure of RGII is generally highly conserved between different sources [93].

Arabinan, a neutral side chain in RGI, is a polymer of $1 \rightarrow 5$ -linked α -L-arabinofuranoside repeating units forming the backbone with substituents of arabinose (single or double) with $1 \rightarrow 2$ and/or $1 \rightarrow 3$ linkages. Arabinogalactan occurs in two types, I and II. Arabinogalactan I (AGI) has a backbone of galactose residues with $1 \rightarrow 4$ linkages with arabinose substituted on the O-3. Arabinogalactan II also contains a galactose backbone, but with $1 \rightarrow 3$ linkages and side chains of arabinose and galactose [92].

Table 3Relative proportions (%) of different structural elements of pectin from different sources [92].

	Black currant	Bilberry	Grape	Soybean	Sugar beet	Apple
Homogalacturonan	68	65	65	0	29	36
Xylogalacturonan	0	0	n.a.	21	< 1	4
RGI	5	6	10	15	4	1
Neutral side chains	24	27	23	60	48	47
RGII	3	2	2	4	4	10

These structural elements have all been isolated from plant cell walls and different models have been proposed to explain how these elements fit together. The prevailing models characterise pectin as having smooth and hairy regions with the smooth regions representing the HG and the hairy regions the RG [92]. Evidence demonstrated that the HG is covalently attached to the RGI and RGII and the neutral sugars form side-chains on the hairy regions [92].

The composition of pectins may differ depending on the source of the pectin. Table 3 provides the relative proportions of the different structural elements in different fruits [92].

It should be noted that traditional methods of pre-treatment, intended to remove lignin, may also remove a large quantity of the pectin present in fruit waste. Different structural elements of pectin can be removed through hot water, weak acid, weak alkali and ammonium oxalate [94]. If the polysaccharides in fruit waste are to be studied in an intact form, pre-treatment conditions must be designed to retain the pectic polysaccharides.

2.2.2. The structure of xyloglucan

Xyloglucans have a backbone of β-1,4 linked glucose residues, similar to cellulose. Some of the glucose residues are substituted with α -D-xylose residues at the C-6 position. The extent of xylose substitution differs from source to source [95]. Additional residues may also be linked to the xylose substituents or to the backbone, depending on the source of the xyloglucan. For example, galactose, fucose, arabinose or a second xylose residue may be linked to the xylose substituent. By convention, a xylose-substituted residue is referred to as X, while an unsubstituted glucose is referred to as G [96]. A glucose substituted by a galactose and xylose disaccharide $(\beta-D-Galp-(1\rightarrow 2)-\alpha-D-Xylp-(1\rightarrow 6)-\beta-D-Glcp)$ is referred to as L and a glucose substituted by a fucose, galactose and xylose trisaccharide $(\alpha-L-Fucp-(1\rightarrow 2)-\beta-D-Galp(1\rightarrow 2)-\alpha-D-Xylp-(1\rightarrow 6)-\beta-D-Galp(1\rightarrow 6)-\alpha-D-Xylp-(1\rightarrow 6)-\beta-D-Galp(1\rightarrow 6)-\alpha-D-Xylp-(1\rightarrow 6)-\beta-D-Galp(1\rightarrow 6)-\alpha-D-Xylp-(1\rightarrow 6)-\alpha-D-Xylp-(1\rightarrow$ D-Glcp) is referred to as F. Thus different xyloglucans can be described as XXXG, XXGG, XXLG, XLXG or XLFG. A more detailed explanation of the nomenclature and structural elements of xyloglucans can be found in Fry et al. [97].

2.2.3. The structure of glucuronoxylan

Glucuronoxylan is the main hemicellulose in olive waste. It consists of a β -1 \rightarrow 4-linked xylopyranosyl backbone [73,74]. The xylose residues contain frequent substituents of glucuronic acid and 4-O-methyl glucuronic acid. Other substituents may include arabinofuranosyl groups [98] or acetyl groups at about 70% of the xylose residues as a substituent at the C-2 or C-3 position [94].

3. Enzymatic bioconversion of polysaccharides in fruit and vegetable waste

3.1. Factors affecting enzymatic lignocellulose bioconversion

Lignocellulose is highly recalcitrant to enzymatic hydrolysis due to various factors, including the presence of lignin, cellulose crystallinity and particle size [99,100]. Food wastes, in some cases, contain very high lignin content. For example, grape stalks and seeds can contain more than 60% lignin [32], palm date fibres (50% lignin) [82], cherry pomace (69.4% lignin) and black currant (59.3% lignin) [22]. The presence of lignin is considered one of the biggest obstacles to the degradation of lignocellulose substrates [101,102]. Many reasons have been put forward for the effect of lignin on hydrolysis of the substrate [103], but it has been established that the lignin has to be removed, modified or disrupted in order to achieve complete hydrolysis of the substrate. This is generally achieved through pre-treatment strategies, which may utilise physical (mechanical, thermal) or chemical (acid, alkaline, ionic

liquid) methods. Several extensive reviews are available on pretreatments [104,99,100,105]. Pre-treatments also have an impact on cellulose crystallinity as well as particle size. Hendriks and Zeeman [99] have reviewed different types of pre-treatment strategies that lead to improved digestibility of lignocellulose, and have also indicated how the type of pre-treatment affects processes such as ethanol, methane and biogas production.

The simplest form of pre-treatment is milling of the lignocellulose which causes a reduction in particle size and crystallinity, thereby increasing the available surface area [99]. Thermal pre-treatment involves heating of the lignocellulose above 150 $^{\circ}$ C. Variations on the process include utilisation of liquid hot water, steam treatment and steam explosion and ammonium fibre expansion. SO₂ and CO₂ explosion have also been used very effectively as a pre-treatment to improve subsequent enzymatic hydrolysis [106].

Chemical pre-treatments include the use of acid or alkaline methods, although this may create compounds such as furfural which is inhibitory to yeasts involved in alcoholic fermentation [99]. Further pre-treatment methods include the use of ionic liquids to disrupt the lignocellulose structure [99]. The use of supercritical CO_2 pre-treatment of lignocellulose has also been explored as an environmentally friendly method [107].

3.2. Enzymes required to degrade polysaccharides in food waste

Various enzymes are required to degrade different polysaccharides to its monomer. Cellulose degradation requires endoglucanases (EC 3.2.1.4), exo-glucanases that can act from both the reducing (EC 3.2.1.176) and non-reducing ends (EC 3.2.1.91), forming cellobiose which is then cleaved into glucose monomers by β -glucosidases (EC 3.2.1.21). Since cellulose forms a large component of the polysaccharides in fruit waste, these enzymes will all be required for the cellulose hydrolysis into monomers [108.109].

The other major component of fruit waste is pectin which consists of different structural features as described. Various enzymes, backbone as well as side-chain cleaving enzymes, can act on bonds found within pectin, such as methyl esterase (EC 3.1.1.11), acetyl esterase (EC 3.1.1.72), pectate lyase (EC 4.2.2.2), pectin lyase (EC 4.2.2.10), endo-polygalacturonase (EC 3.2.1.15), exo-polygalacturonase (EC 3.2.1.67 and EC 3.2.1.82) rhamnogalacturonan lyase (EC 4.2.2), rhamnogalacturonan hydrolase (EC 3.2.1), rhamnogalacturonan rhamnohydrolase (EC 3.2.1.174), endoxylogalacturonan hydrolase (EC 3.2.1), rhamnogalacturonan galacturono hydrolase, arabinase (EC 3.2.1.99), endo-galactanase (EC 3.2.1.89) (incomplete EC numbers indicate that the enzymes have not been classified yet). Some of these enzymes and their specificities have been described in Voragen et al. [92]. It should be noted that α -1,4-endo-polygalacturonase, used on its own, can release approximately 50% of homogalacturonan, 33% of RGI and 100% of RGII from plant cell walls [94]. This is achieved by cleavage of the backbone of the galacturonic acid polymer.

Many endo-glucanases, but not all, are able to cleave the xyloglucan backbone at unsubstituted glucose residues. For example, EG I and EG III from *Trichoderma reesei* can do this, but not EG II [96]. The ability of endo-glucanases to cleave the xyloglucan backbone can depend on the particular substitutions on the backbone as certain adjacent substituents can prevent the endo-glucanase from acting on the unbranched glucose in the backbone [94]. Very specific enzymes have been isolated that can only act on xyloglucan, a xyloglucan-specific endo- β -1,4-glucanase (EC 3.2.1.151) [96]. The enzyme isolated by Grishutin et al. [96] displayed no activity towards carboxymethylcellulose (CMC). Removal of the xylose substituents requires a further enzyme, an α -xylosidase [110]. Xyloglucan can be released from cells by an

alkali treatment; therefore any pre-treatments to remove lignin and which utilise alkaline chemicals will most likely also remove the xyloglucan hemicellulose to some extent.

Glucuronoxylan can be degraded through the action of endo- β -1,4-xylanases (EC 3.2.1.8), β -xylosidase (EC 3.2.1.37) and α -glucuronidase (EC 3.2.1.139). Acetyl groups on the xylan backbone have to be removed using an acetyl xylan esterase (EC 3.2.1.72). Not all endo-xylanases can cleave the glucuronoxylan backbone and glucuronoxylan-specific xylanases have been isolated [111].

3.3. Interactions and associations between polysaccharides in food waste and their impact on enzymatic bioconversion

In native lignocellulose substrates, interactions and associations exist between plant polysaccharides which affect the overall hydrolysis of the cell wall by hydrolytic enzymes. Some of the synergy studies using hydrolytic enzymes and lignocellulose substrates, such as grass or wood, have revealed some of these associations and interactions. Thus it has been established that xylan associates with cellulose microfibrils through hydrogen bonding interactions. The xylan therefore masks the cellulose and prevents access of cellulases to their substrate, thus posing an obstacle to the hydrolysis of the cellulose [112,113]. In some cases it has also been established that the cellulose masks the xylan in a similar manner [114]. Thus, utilisation of cellulases and xylanases simultaneously, promotes the hydrolysis of both substrates through cooperative degradation. Some studies also suggest that xylan and mannan, as well as cellulose and mannan, associate with each other in some manner which prevents their hydrolysis unless enzymes are used in combination [115,116]. Enzymes can therefore have a direct effect on the increased hydrolysis of a polysaccharide that is not their own substrate. Understanding the associations may therefore assist us in selection of enzyme combinations for deconstruction of a substrate to its monomers.

Apart from cellulose, the other polysaccharides food waste differs substantially from other lignocellulose sources and therefore different interactions and associations can be expected. For example, xyloglucan has been demonstrated to interact with cellulose through hydrogen bonding, probably in a similar manner to arabinoxylan [117]. The xyloglucan functions "to coat and tether cellulose microfibrils" [118]. However, the association with cellulose may vary depending on the specific sidechains on the xyloglucan backbone [119]. It is thus expected that this association may influence the degradation of both the cellulose and xyloglucan substrates by their enzymes.

Further interactions have also been studied between pectin and cellulose. Thus it has been established that pectin forms hydrogen bonds with cellulose, specifically through neutral arabinan and galactan sidechains found in rhamnogalacturonan I. Zykwinska et al. [120] found that this interaction was so strong that arabinan and galactan hydrolysing enzymes were unable to hydrolyse these sidechains in the presence of cellulose. Where xyloglucan as well as RGI is present in a plant cell, the xyloglucan will bind preferentially to the cellulose. In lignocellulose with low xyloglucan, but high pectin (such as sugar beet, celery, onion and carrot) there is competitive binding to the cellulose [120]. It was also demonstrated that arabinan sidechains only interacted with cellulose where more than 10 arabinose residues were present. Therefore the specific nature of the sidechains will influence their association with the cellulose.

No association between rhamnogalacturonan II and other polysaccharides have been reported, apart from its covalent linkage with homogalacturonan. The ability of endo-polygalacturonase to release 100% of RGII [94], thus cleaving this covalent linkage, probably indicates that RGII is not associated with any other polysaccharide or only loosely associated.

Coimbra et al. [121] also indicated that an association existed between glucuronoxylan and xyloglucan in olive pulp. It is not clear what the nature of this association may be. Thompson and Fry [122] also indicated that xyloglucan was covalently attached to acidic residues in pectin in rose cells.

Arnous and Meyer [123] also indicated that arabinan and galactan sidechains contained ester linkages with phenolics. There also appears to be some interaction between tannins and polysaccharides, although the type of interaction is not clear. Baciu and Jordening [23] also indicated that ferulic acid linkages exist between arabinan and galactan sidechains. According to Caffall and Mohnen [118] dimeric ferulic acid linkages serve to link different RGI molecules through different arabinan sidechains.

The effect of these associations on the hydrolysis of the substrate can be determined through enzyme synergy studies using pure enzymes. The presence of synergy will indicate a level of cooperation between enzymes which would give evidence of the effect of associations.

3.4. Enzyme synergism

Synergism between enzymes is a reflection of the degree of cooperation that two or more enzymes display in the degradation of a substrate. The degree of synergy (DS) is a value calculated by dividing the observed activity of a combination of enzymes with the theoretical sum of the individual activities of the same enzymes on the same substrate. The DS values can be divided into three categories. A DS of greater than one is a clear indication that synergy took place and that the enzyme combination displayed enhanced activity. A greater value of calculated DS indicates a larger cooperation between the enzymes. A DS of 1 indicates that no synergy took place between the enzymes and that the enzymes were able to act on the substrate without any cooperation. A DS of less than one is an indication that no synergy occurred and that enzymes were probably competing with each other for binding sites on the substrate [103].

The degree of synergy is therefore a valuable parameter to study the interactions between enzymes, and to understand interactions and associations between different polysaccharides within the substrate. Therefore synergy studies may assist in determination of the enzymes required in designer cocktails for lignocellulose degradation. However, the observation of synergy may only take place under certain circumstances and is influenced by several factors, including time and the concentration of the enzymes [103].

3.5. Enzyme bioconversion or synergy studies on food waste (pectin containing substrates)

Extensive enzyme synergy studies have been conducted on lignocellulose substrates such as corn stover, grasses and wood (see review by Van Dyk and Pletschke [103]). However, we have demonstrated that food wastes have different polysaccharide compositions and different interactions, and therefore further studies have to be conducted on the food wastes.

Several studies have used purified enzymes or commercial enzyme mixtures for the degradation of fruit waste, but very few examined synergistic relationships between enzymes. Capek et al. [124] investigated the activity of pectin lyase and endoglucanase, individually and combined, on apple cell walls and found synergistic cooperation between these enzymes. When used in combination, the yield of sugars was higher than when the enzymes were used individually. The authors reasoned that the synergy was probably "due to the increase in the extraction of hairy regions of the pectin compounds" [124]. It is interesting to note that lower

levels of glucose appeared to be extracted when the enzyme combination was used, compared to the use of the endoglucanase alone. It is not clear why this would be the case.

Pakarinen et al. [125] investigated the role of pectinases to increase enzymatic hydrolysis of hemp. The addition of pectinases (Pectinex) with cellulases (Celluclast and Novozyme 188) increased the hydrolysis yield of hemp (*Cannabis sativa* L.) compared to using the cellulase alone. The authors concluded that the removal of pectin improved the accessibility of enzymes by improving the substrate surface area and therefore increased the hydrolysis of cellulose. Pectin removal appears to "result in disassembly of fibre bundles" and results in larger pores, giving greater access to enzymes. The addition of pectinases increased the amount of galacturonic acid produced, as well as the amount of neutral sugar produced.

Spagnuolo et al. [5] used three cellulases, one hemicellulase and three pectinases on sugar beet pulp in different combinations of two or three enzymes. Synergistic cooperation was found between the different enzymes in the release of total monosaccharides, with individual sugars such as glucose, arabinose and galacturonic acid release measured separately. The authors concluded that hydrolysis of the pectins "favoured the degradation of cellulose and hemicellulose" [5]. The results seem to suggest that pectins are associated with the cellulose and hemicellulose in the substrate and that the cooperation between the enzymes improves hydrolysis.

Bonnin et al. [29] investigated the hydrolysis of sugar beet pulp with a sequential treatment of pectinases, followed by a cellulase treatment. In this manner, up to 64% of the cellulose in the pulp was hydrolysed. This suggests that the pectin masks the cellulose and thus limits the hydrolysis of the cellulose by cellulases.

The presence of synergistic behaviour between pectinases and cellulases confirm that associations exist between the polysaccharides in the substrate which prevent their hydrolysis by individual enzymes. These associations influence the ability of enzymes to degrade their specific substrates as the one type of polysaccharide appears to prevent access of enzymes to the other (polysaccharide). However, the number of studies that have used synergistic cooperation between enzymes to elucidate the effect of these associations on hydrolysis of the substrate are very limited, particularly as only two different substrates have been investigated. Further studies should be carried out with different enzyme combinations on different substrates to give us greater insight into the effect of associations between polysaccharides on the overall hydrolysis of the substrate.

Further studies may explore some of the following questions:

- Is the synergy between pectinases and cellulases sequential or simultaneous? Therefore, must the pectin be removed first before the cellulases can act on the cellulose (sequential)? Or does the cellulose also hamper access of the pectinases to their substrate? (which was found in the interaction between xylan and cellulose [114]). Experiments that may shed light on this relationship could examine the type of synergy, but also investigate the relationship between the release of galacturonic acid and glucose.
- What is the relationship between pectin and other hemicelluloses? Only one study has examined the effect of hemicellulases in pectin containing substrates [5].
- What impact does the presence of xyloglucan have on the hydrolysis of cellulose?
- If the pectin only interacts with the cellulose through arabinan and galactan sidechains, what would be the impact of arabinase or galactanase enzymes in the presence of cellulases?
- As arabinan sidechains are linked through ferulic acid ester linkages, what impact would a ferulic acid esterase have on release of arabinose from the arabinan.

Several studies have investigated the use of glycoside hydrolase enzymes to release phenolics from fruit waste which is generally carried out by chemical means [66]. Arnous and Meyer [123] used commercial enzyme mixtures (Celluclast, Pectinex and Vinozyme) and examined the release of phenolics and anthocyanins from grape pomace. A linear correlation was found between the release of total phenols and carbohydrate degradation. The greatest release of phenols was found using pectinases. This study therefore revealed that there is a relationship between carbohydrate degradation and release of phenolics. There is therefore an association between the phenolics and polysaccharides in food waste which affects the degradation of the substrate and could be further investigated. Costoya et al. [66] found a synergistic cooperation between enzymes in the release of phenolics from grape pomace using Cellubrix, Neutrase and Viscozyme.

The use of commercial enzyme mixtures with multiple and unknown enzymes makes it difficult to determine which enzymes interacted to produce the results and individual enzymes may give a greater insight into these interactions. However, if enzyme mixtures can release phenolics from fruit waste while hydrolysing polysaccharides, the phenolics can be separated from the sugars as an additional value-added product. However, it has been established that the phenolic compounds from degradation can inhibit hydrolytic enzymes. Therefore, the particular phenolics resulting from fruit waste would also have to be examined for their effect on enzyme activity.

4. Products from enzymatic bioconversion of fruit and vegetable waste and challenges for fermentation

In the hydrolysis of the lignocellulose component of food waste, many different products may be produced, including glucose, galacturonic acid, arabinose, galactose, rhamnose, xylose, mannose and fucose. Unlike other lignocellulose feedstocks such as grass or wood, the production of food waste also results in high levels of free sugars such as fructose, adding additional, readily available substrates for ethanol production.

Utilisation of these products for bioethanol fermentation requires conversion by a yeast or bacterium. The main organism utilised for bioethanol fermentation has been Saccharomyces cerevisiae. However, this organism has a disadvantage in that it can only ferment hexose sugars. This would result in an underutilisation of the available monomer products, such as arabinose, and potentially lower yields of ethanol. If all the sugars could be utilised for bioethanol production, higher yields of ethanol can be obtained to improve the economic sustainability of the bioconversion process. Reviews on organisms, other than S. cerevisiae, able to ferment other sugars are provided in Kuhad et al. [126] and Dien et al. [61]. Various species of yeasts and bacteria have been investigated for fermentation of pentose sugars such as Candida shehatae, Pichia stipitis and Pachysolen tannophilus (yeasts), Bacillus macerans, Bacillus polymyxa, Klebsiella pneumoniae, Clostridium acetobutylicum, Aeromonas hydrophila, Aerobacter sp., Erwinia sp., Escherichia sp., Leuconostoc sp., Lactobacillus sp., Thermoanaerobacterium saccharolyticum, and Z. mobilis (bacteria) [126]. Although there are some problems associated with these organisms, such as slow fermentation rates and sensitivity to inhibitors, many of these attributes can be improved through genetic engineering. Some of the approaches in this regard are discussed by Dien et al. [61]. Z. mobilis is already capable of fermenting fructose, glucose and sucrose, while genetic engineering has been able to produce strains that are also able to ferment arabinose and xylose [61].

Limited reports in literature have investigated the fermentation of galacturonic acid into ethanol. Grohmann et al. [127–129] investigated the fermentation of galacturonic acid by *E. coli*

KO11, Erwinia crysanthemi EC16 and Erwinia carotovora SR38. Orange peel was hydrolysed using a combination of Pectinex Ultra SP, Celluclast 1.5 L and Novozyme 188 and thereafter the neutral sugars and galacturonic acid were fermented into ethanol utilising these strains. The E. coli KO11 could successfully metabolise arabinose and galacturonic acid [127,128], while the Erwinia species also utilised glucose. Conversion of galacturonic acid produced equimolar amounts of ethanol and acetate, as well as carbon dioxide.

5. Conclusion and future prospects

Very high quantities of food waste are produced worldwide annually. Many valuable compounds can be extracted from this waste, such as pectin, dietary fibre, phenolics and other antioxidants. However, a large part of this waste, the lignocellulose, remains largely underutilised and could serve as a feedstock for bioethanol production. Utilisation for this purpose requires an understanding of the composition of the lignocellulose fraction and, specifically, the structure of different polysaccharides within the lignocellulose fraction. This will allow the selection of the appropriate enzymes required to degrade these polysaccharides. Furthermore, the associations between polysaccharides have to be better understood as they may pose an obstacle to the degradation of the polysaccharides. As a large variety of sugar monomers will form as products of the hydrolysis of these polysaccharides, alternative fermentation strategies may have to be considered. Certain food processing wastes may also contain compounds that may be inhibitory to the fermentation process and this has to be taken into account.

Before food wastes can be fully utilised, future work has to address certain gaps in the current knowledge. More extensive analysis of polysaccharide composition of food wastes have to be carried out, particularly detailed structural analysis of the polysaccharides. To achieve a greater understanding of associations between polysaccharides, advanced synergy studies should be carried out to provide an insight into associations and areas of recalcitrance caused by these associations. Synergy studies using pure enzymes will also allow us to design optimal combinations of enzymes for complete hydrolysis of these substrates. The impact of phenolics and other compounds, found in these substrates, on the hydrolytic enzymes should also be further investigated. Due to the high pectin content of these substrates, galacturonic acid will be one of the main products formed and therefore options for its fermentation should be explored as very little work has been carried out in this regard.

Acknowledgements

The authors would like to thank the Water Research Commission (WRC) of South Africa and Rhodes University for funding.

References

- [1] FAO—Food and Agricultural Organisation of the United Nations; 2012. \(\lambda\text{ttp://faostat.fao.org}\rangle.\)
- [2] Gullón B, Falqué E, Alonso JL, Parajó JC. Evaluation of apple pomace as a raw material for alternative applications in food industries. Food Technology and Biotechnology 2007;45(4):426–33.
- [3] Wilkins MR, Widmer WW, Grohmann K, Cameron RG. Hydrolysis of grapefruit peel waste with cellulase and pectinase enzymes. Bioresource Technology 2007;98:1596–601.
- [4] Attri BL, Maini SB. Extraction of pectin from galgal fruit peel. Bioresource Technology 1996;55:89–91.
- [5] Spagnuolo M, Crecchio C, Pizzigallo MDR, Ruggiero P. Synergistic effects of cellulolytic and pectinolytic enzymes in degrading sugar beet pulp. Bioresource Technology 1997;60:215–22.

- [6] Fernández-Bolaños J, Jiménez A. Steam-explosion of olive stones: hemicellulose solubilisation and enhancement of enzymatic hydrolysis of cellulose. Bioresource Technology 2001;79:53-61.
- Schieber A, Stintzing FC, Carle R. By-products of plant food processing as a source of functional compounds recent developments. Trends in Food Science & Technology 2001;12:401-13.
- [8] Bardiya N, Somayaji D, Khanna S. Biomethanation of banana peel and pineapple waste. Bioresource Technology 1996;58:73-6.
- Emaga TH, Robert C, Ronkart SN, Wathelet B, Paquot M. Dietary fibre components and pectin chemical features of peels during ripening in banana and plantain varieties. Bioresource Technology 2008;99:4346-54
- [10] Ban-Koffi L, Han YW. Alcohol production from pineapple waste. World Journal of Microbiology and Biotechnology 1990;6:281-4.
- [11] Joshi VK, Attri D. Solid state fermentation of apple pomace for the production of value added products. Natural Product Radiance 2006;5(4):289–96.
- [12] Laufenberg G, Kunz B, Nystroem M. Transformation of vegetable waste into value added products: (A) the upgrading concept; (B) practical implementations. Bioresource Technology 2003;87:167-98.
- [13] Shalini R, Gupta DK. Utilisation of pomace from apple processing industries: a review. Journal of Food Science and Technology 2010;47:365-71.
- Arslan Y, Eken-Saracoglu N. Effects of pre-treatment methods for hazelnut shell hydrolysate fermentation with Pichia stipitis to ethanol. Bioresource Technology 2010;101:8664-70.
- [15] Lohrasbi M, Pourbafrani M, Niklasson C, Taherzadeh MJ. Process design and economic analysis of a citrus waste biorefinery with biofuels and limonene as products. Bioresource Technology 2010;101:7382-8.
- [16] Villas-Boas SG, Esposito E, Matos de Mendonca M. Bioconversion of apple pomace into a nutritionally enriched substrate by Candida utilis and Pleurotus ostreatus. World Journal of Microbiology and Biotechnology 2003;19:
- [17] Arvanitoyannis IS, Ladas D, Mavromatis A. Potential uses and applications of treated wine waste: a review. International Journal of Food Science and Technology 2006;41:475-87.
- [18] Haddadin MS, Haddadin J, Arabiyat OI, Hattar B. Biological conversion of olive pomace into compost by using Trichoderma harzianum and Phanerochaete chrysosporium. Bioresource Technology 2009;100:4773-82.
- [19] Bhushan S, Kalia K, Sharma M, Singh B, Ahuja PS. Processing of apple pomace for bioactive molecules. Critical Reviews in Biotechnology 2008;28:285-96.
- [20] Funami T, Nakauma M, Ishihara S, Tanaka R, Inoue T, Phillips GO. Structural modifications of sugar beet pectin and the relationship of structure to functionality. Food Hydrocolloids 2011;25:221–9.
- [21] Marin FR, Soler-Rivas C, Benavente-Garcia O, Castillo J, Perez-Alvarez JA. By-product from different citrus processes as a source of customized functional fibres. Food Chemistry 2007;100:736–41.
- [22] Nawirska A. Kwasniewska M. Dietary fibre fractions from fruit and vegetable processing waste. Food Chemistry 2005;91:221–5.
- [23] Baciu I-E, Jordening H-J. Kinetics of galacturonic acid release from sugar-beet pulp. Enzyme and Microbial Technology 2004;34:505-12.
- [24] Deng Q, Penner MH, Zhao Y. Chemical composition of dietary fiber and polyphenols of five different varieties of wine grape pomace skins. Food Research International 2011;44:2712–20.
- [25] Mei X, Mu T-H, Han J-J. Composition and physicochemical properties of dietary fiber extracted from residues of 10 varieties of sweet potato by a sieving method. Journal of Agricultural and Food Chemistry 2010;58:7305-10.
- [26] Cetkovic G, Canadanovic-Brunet J, Djilas S, Savatovic S, Mandic A, Tumbas V. Assessment of polyphenolic content and in vitro antiradical characteristics of apple pomace. Food Chemistry 2008;109:340-7.
- Arnous A, Meyer AS. Comparison of methods for compositional characterisation of grape (Vitis vinifera L.) and apple (Malus domestica) skins. Food and Bioproducts Processing 2008;86:79-86.
- [28] Zuorro A, Fidaleo M, Lavecchia R. Enzyme-assisted extraction of lycopene from tomato processing waste. Enzyme and Microbial Technology 2011;49:567-73.
- [29] Bonnin E, Grange H, Lesage-Meessen L, Asther M, Thibault J-F. Enzymic release of cellobiose from sugar beet pulp, and its use to favour vanillin production in Pycnoporus cinnabarinus from vanillic acid. Carbohydrate Polymers 2000;41:143-51.
- [30] Muheim A, Lerch K. Towards a high-yield bioconversion of ferulic acid to vanillin. Applied Microbiology and Biotechnology 1991;51:456-61.
- [31] Nolleau V, Preziosi-Belloy L, Delgenes JP, Navarro JM. Xylitol production from xylose by two yeast strains: sugar tolerance. Current Microbiology 1993;27:191-7.
- [32] Botella C, de Ory I Webb C, Cantero D, Blandino A. Hydrolytic enzyme production by Aspergillus awamori on grape pomace. Biochemical Engineering Journal 2005;26:100-6.
- [33] Cheilas T, Stoupis T, Christakopoulos P, Katapodis P, Mamma D, Hatzinikolaou DG, et al. Hemicellulolytic acitivity of Fusarium oxysporum grown on sugar beet pulp. Production of extracellular arabinanase. Process Biochemistry 2000;35:557-61.
- [34] Dhillon GS, Kaur S, Brar SK, Verma M. Potential of apple pomace as a solid substrate for fungal cellulase and hemicellulase bioproduction through solid-state fermentation. Industrial Crops and Products 2012;38:6-13.
- Pourbafrani M, Forgacs G, Horvath IS, Niklasson C, Taherzadeh MJ. Production of biofuels, limonene and pectin from citrus wastes. Bioresource Technology 2012;101:4246-50.
- Sun J. D-limonene: safety and clinical applications. Alternative Medicine Review 2007;12(3):259-63.

- [37] Menon V, Rao M. Trends in bioconversion of lignocellulose: biofuels, platform chemicals & biorefinery concept. Progress in Energy and Combustion 2012:38:522-50.
- [38] Dora S, Bhaskar T, Singh R, Naik DV, Adhikari DK. Effective catalytic conversion of cellulose into high yields of methyl glucosides over sulfonated carbon based catalyst. Bioresource Technology 2012;120:318-21.
- [39] Guo H, Qi X, Li L, Smith Jr RL. Hydrolysis of cellulose over functionalized glucose-derived carbon catalyst in ionic liquid. Bioresource Technology 2012:116:355-9.
- [40] Yang H, Shao P, Lu T, Shen J, Wang D, Xu Z, et al. Continuous bio-hydrogen production from citric acid wastewater via facultative anaerobic bacteria. International Journal of Hydrogen Energy 2006;31:1306–13.
- [41] Wang H, Wang J, Fang Z, Wang X, Bu H. Enhanced bio-hydrogen production by anaerobic fermentation of apple pomace with enzyme hydrolysis. International Journal of Hydrogen Energy 2010;35:8303-9.
- [42] Kapdan IK, Kargi F. Bio-hydrogen production from waste materials. Enzyme and Microbial Technology 2006;38:569-82.
- [43] Oh YK, Scol EH, Kim MS, Park S. Photoproduction of hydrogen from acetate by chemoheterotrophic bacterium Rhodopseudomonas palustris P4. International Journal of Hydrogen Energy 2004;29:1115-21.
- Yokoi H, Saitsu AS, Uchida H, Hillrose J, Hayashi S, Takasaki Y. Microbial hydrogen production from sweet potato starch residue. Journal of Bioscience and Bioengineering 2001;91:58-63.
- [45] Yokoi H, Mori S, Hillrose J, Hayashi S, Takasaki Y. H₂ production from starch by mixed culture of Clostridium butyricum and Rhodobacter sp. M-19. Biotechnology Letters 1998;20(9):895-9.
- [46] Feng X, Wang H, Wang Y, Wang X, Huang J. Biohydrogen production from apple pomace by anaerobic fermentation with river sludge. International Journal of Hydrogen Energy 2009;30:1-7.
- [47] Kothari R, Tyagi VV, Pathak A. Waste-to-energy: a way from renewable energy 8sources to sustainable development. Renewable and Sustainable Energy Reviews 2010;14:3164-70.
- [48] Cuzin N, Farinet J, Segretain C, Labat M. Methanogenic fermentation of cassava peel using pilot plug flow digester. Bioresource Technology 1992;41:259–64.
- [49] Kalia VC, Kumar A, Jain SR, Joshi AP. Biomethanation of plant materials. Bioresource Technology 1992;41:209–12.
- [50] Somayaji D. Biomethanation of rice and wheat straw. World Journal of Microbiology and Biotechnology 1992;10:521-3.
- [51] Prema V, Devi S, Nand K. Anaerobic digestion of fruit and vegetable processing wastes for biogas production. Bioresource Technology 1992;40:43-8.
- [52] Hammond JB, Egg R, Diggins D, Coble CG. Alcohol from bananas. Bioresource
- Technology 1996;56:125–30.
 [53] Oberoi HS, Vadlani PV, Saida L, Bansal S, Hughes JD. Ethanol production from banana peels using statistically optimized simultaneous saccharification and fermentation process. Waste Management 2011;31:1576–84.
- [54] Tewari HK, Marwaha SS, Rupal K. Ethanol from banana peels. Agricultural Waste 1986:16:135-46
- Rodriguez LA, Toro ME, Vazquez F, Correa-Daneri ML, Gouiric SC, Vallejo MD. Bioethanol production from grape and sugar beet pomaces by solid-state fermentation. International Journal of Hydrogen Energy 2010;35:5914-7.
- [56] Korkie LJ, Janse BJH, Viljoen-Bloom M. Utilising grape pomace for ethanol production. South African Journal of Enology and Viticulture 2002;23:31–6.
- [57] Arapoglou D, Varzakas T, Vlyssides A, Israilides C. Ethanol production from potato peel waste (PPW). Waste Management 2010;30:1898-902.
- [58] Boluda-Aguilar M, Garcia-Vidal L, Gonzalez-Castaneda FP, Lopez-Gomez A. Mandarin peel wastes pre-treatment with steam explosion for bioethanol production. Bioresource Technology 2010;101:3506-13.
- [59] Oberoi HS, Vadlani PV, Nanjundaswamy A, Bansal S, Singh S, Kaur S, et al. Enhanced ethanol production from Kinnow mandarin (Citrus reticulata) waste via a statistically optimized simultaneous saccharification and fermentation process. Bioresource Technology 2011;102:1593-601.
- [60] Balat M. Production of bioethanol from lignocellulosic materials via the biochemical pathway: a review. Energy Conversion and Management 2011;52:858-75.
- [61] Dien BS, Cotta MA, Jeffries TW. Bacteria engineered for fuel ethanol production: current status. Applied Microbiology and Biotechnology 2003;63:258–66. [62] Le Bourvellec C, Bouzerzour K, Ginies C, Regis S, Ple Y, Renard CM. Phenolic
- and polysaccharidic composition of applesauce is close to that of apple flesh. Journal of Food Composition and Analysis 2011;24:537-47.
- [63] Massiot P, Baron A, Drilleau JF. Characterisation and enzymatic hydrolysis of cell-wall polysaccharides from different tissue zones of apple. Carbohydrate Polymers 1994;25:145-54.
- [64] Prabasari I, Pettolino F, Liao M-L, Bacic A. Pectic polysaccharides from mature orange (Citrus sinensis) fruit albedo cell walls: sequential extraction and chemical characterization. Carbohydrate Polymers 2011;84:484-94.
- [65] Widmer W, Zhou W, Grohmann K. Pre-treatment effects on orange processing waste for making ethanol by simultaneous saccharification and fermentation. Bioresource Technology 2010;101:5242-9.
- [66] Costoya N, Sineiro J, Pinelo M, Rubilar M, Nunez MJ. Enzyme-aided extraction of polyphenols from grape pomace. Electronic Journal of Environmental, Agricultural and Food Chemistry 2010;9(4):696-705.
- Lecas M, Brillouet J-M. Cell wall composition of grape berry skins. Phytochemistry 1994;35(5):1241-3
- [68] Ping L, Brosse N, Sannigrahi P, Ragauskas A. Evaluation of grape stalks as a bioresource. Industrial Crops and Products 2011;33:200-4.

- [69] Prozil SO, Evtuguin DV, Lopes LP. Chemical composition of grape stalks of Vitis vinifera L. from red grape pomaces. Industrial Crops and Products 2012;35:178–84.
- [70] Spigno G, Pizzorno T, De Faveri DM. Cellulose and hemicelluloses recovery from grape stalks. Bioresource Technology 2008;99:4329–37.
- [71] Vidal S, Williams P, O'Neill MA, Pellerin P. Polysaccharides from grape berry cell walls. Part I: tissue distribution and structural characterisation of the pectic polysaccharides. Carbohydrate Polymers 2001;45:315–23.
- [72] Chamorro S, Viveros A, Alvarez I, Vega E, Brenes A. Changes in polyphenol and polysaccharide content of grape seed extract and grape pomace after enzymatic treatment. Food Chemistry 2012;133:308–14.
- [73] Fernandez-Bolanos J, Felizon B, Heredia A, Guillen R, Jimenez A. Characterization of the lignin obtained by alkaline delignification of the cellulose residue from steam-exploded olive stones. Bioresource Technology 1999;68:121–32.
- [74] Mafra I, Barros AS, Coimbra MA. Effect of black oxidising table olive process on the cell wall polysaccharides of olive pulp (*Olea europaea* L. var. Negrinha do Douro). Carbohydrate Polymers 2006;65:1–8.
- [75] Rodriguez G, Lama A, Rodriguez R, Jimenez A, Guillen R, Fernandez-Bolanos J. Olive stone is an attractive source of bioactive and valuable compounds. Bioresource Technology 2008;99:5261–9.
- [76] Vierhuis E, Schols HA, Beldman G, Voragen AG. Isolation and characterisation of cell wall material from olive fruit (*Olea europaea* cv koroneike) at different ripening stages. Carbohydrate Polymers 2000;43:11–21.
- [77] Chamy R, Illanes A, Aroca G, Nunez L. Acid hydrolysis of suar beet pulp as pre-treatment for fermentation. Bioresource Technology 1994;50:149–52.
- [78] Dinand E, Chanzy H, Vignon MR. Suspensions of cellulose microfibrils from sugar beet pulp. Food Hydrocolloids 1999;13:275–83.
- [79] Micard V, Renard CM, Thibault J-F. Enzymatic saccharification of sugar-beet pulp. Enzyme and Microbial Technology 1996;19:162–70.
- [80] Oosterveld A, Beldman G, Schols HA, Voragen AG. Arabinose and ferulic acid rich pectic polysaccharides extracted from sugar beet pulp. Carbohydrate Research 1996;288:143–53.
- [81] Oosterveld A, Beldman G, Schols HA, Voragen AG. Characterization of arabinose and ferulic acid rich pectic polysaccharides and hemicelluloses from sugar beet pulp. Carbohydrate Research 2000;328:185–97.
- [82] Shafiei M, Karimi K, Taherzadeh MJ. Palm date fibers: analysis and enzymatic hydrolysis. International Journal of Molecular Sciences 2010;11:4285–96.
- [83] Thomassen LV, Larsen DM, Mikkelsen JD, Meyer AS. Definition and characterization of enzymes for maximal biocatalytic solubilization of prebiotic polysaccharides from potato pulp. Enzyme and Microbial Technology 2011;49: 289–97.
- [84] Femenia A, Garcia-Conesa M, Simal S, Rosello C. Characterisation of the cell walls of loquat (*Eriobotrya japonica* L.) fruit tissues. Carbohydrate Polymers 1998;35:169–77.
- [85] Femenia A, Sanchez ES, Simal S, Rossello C. Compositional features of polysaccharides from *Aloe vera (Aloe barbadensis Miller)* plant tissues. Carbohydrate Polymers 1999;39:109–17.
- [86] Habibi Y, Mahrouz M, Vignon MR. Microfibrillated cellulose from the peel of prickly pear fruits. Food Chemistry 2009;115:423–9.
- [87] Hilz H, Bakx EJ, Schols HA, Voragen AG. Cell wall polysaccharides in black currants and bilberries - characterisation in berries, juice, and press cake. Carbohydrate Polymers 2005;59:477–88.
- [88] Hilz H, de Jong LE Kabel MA, Schols HA, Voragen AG. A comparison of liquid chromatography, capillary electrophoresis, and mass spectrometry methods to determine xyloglucan structures in black currants. Journal of Chromatography A 2006;1133:275–86.
- [89] Ribeiro DS, Henriqu SMB, Oliveira LS, Macedo GA, Fleuri LF. Enzymes in juice processing: a review. International Journal of Food Science and Technology 2010;45:635–41.
- [90] Bayer EA, Chanzy H, Lamed R, Shoham Y. Cellulose, cellulases and cellulosomes. Current Opinions in Structural Biology 1998;8:548–57.
- [91] Lynd LR, Weimer PJ, Van Zyl WH, Pretorius IS. Microbial cellulose utilization: fundamentals and biotechnology. Microbiology and Molecular Biology Reviews 2002;66(3):506–77.
- [92] Voragen AG, Coenen G-J, Verhoef RP, Schols HA. Pectin, a versatile polysaccharide present in plant cell walls. Structural Chemistry 2009;20:263–75.
- [93] Willats WC, Know JP, Mikkelsen JD. Pectin: new insights into an old polymer are starting to gel. Trends in Food Science & Technology 2006;17:97–104.
- [94] Albersheim P, Darvill A, Roberts K, Sederoff R, Staehelin A. Plant cell walls. From chemistry to biology. New York: Taylor & Francis Group; 2011.
- [95] Fry SC. The structure and functions of xyloglucan. Journal of Experimental Botany 1989;40(210):1–11.
- [96] Grishutin SG, Gusakov AV, Markov AV, Ustinov BB, Semenova MV, Sinitsyn AP. Specific xyloglucanases as a new class of polysaccharide-degrading enzymes. Biochimica et Biophysica Acta 2004;1674:268–81.
- [97] Fry SC, York WS, Albersheim P, Darvill A, Hayashi T, Joseleau J-P, et al. An unambiguous nomenclature for xyloglucan-derived oligosaccharides. Physiologia Plantarum 1993;89(1):1–3.
- [98] Reis A, Domingues MRM, Ferrer-Correia AJ, Coimbra MA. Structural characterisation by MALDI-MS of olive xylo-oligosaccharides obtained by partial acid hydrolysis. Carbohydrate Polymers 2003;53:101–7.
- [99] Hendriks AW, Zeeman G. Pre-treatments to enhance the digestibility of lignocellulosic biomass. Bioresource Technology 2009;100:10–8.
- [100] Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, et al. Features of promising technologies for pre-treatment of lignocellulosic biomass. Bioresource Technology 2005;96:673–86.

- [101] Jung H-JG, Jorgensen MA, Linn JG, Engels FM. Impact of accessibility and chemical composition on cell wall polysaccaride degradability of maize and lucerne stems. Journal of the Science of Food and Agriculture 2000;80:419–27.
- [102] Varnai A, Siika-aho M, Viikari L. Restriction of the enzymatic hydrolysis of steam-pretreated spruce by lignin and hemicellulose. Enzyme and Microbial Technology 2010;46:185–93.
- [103] Van Dyk JS, Pletschke BI. A review of lignocellulose bioconversion using enzymatic hydrolysis and synergistic cooperation between enzymes—factors affecting enzymes, conversion and synergy. Biotechnology Advances 2012;30(6):1458–80.
- [104] Chandra RP, Bura R, Mabee WE, Berlin A, Pan X, Saddler JN. Substrate pretreatment: the key to effective enzymatic hydrolysis of lignocellulosics. Advances in Biochemcal Engineering/Biotechnology 2007;108:67–93.
- [105] Sun Y, Cheng J. Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresource Technology 2002:83:1–11.
- [106] Myat L, Ryu G-H. Effect of carbon dioxide injection on physiochemical properties and saccharification of extruded corn starch for fermentation substrate preparation. Microbial & Biochemical Technology 2013;5:18–24.
- [107] Kim KH, Hong J. Supercritical CO₂ pre-treatment of lignocellulose enhances enzymatic cellulose hydrolysis. Bioresource Technology 2001;77:139–44.
- [108] Teeri TT. Crystalline cellulose degradation: new insight into the function of cellobiohydrolases. Trends in Biotechnology 1997;15:160–7.
- [109] Zhang Y-HP, Lynd LR. Toward an aggregated understanding of enzymatic hydrolysis of cellulose: noncomplexed cellulase systems. Biotechnology and Bioengineering 2004;88(7):797–824.
- [110] O'Neill RA, Albersheim P, Darvill AG. Purification and characterization of a xyloglucan oligosaccharide-specific xylosidase from pea seedlings. Journal of Biological Chemistry 1989;264(34):20430–7.
- [111] Nishitani K, Nevins DJ. Glucuronoxylan xylanohydrolase. A unique xylanase with the requirement for appendant glucuronosyl units. Journal of Biological Chemistry 1991:266:6539–43.
- [112] Bura R, Chandra R, Saddler J. Influence of xylan on the enzymatic hydrolysis of steam-pretreated corn stover and hybrid poplar. Biotechnology Progress 2009:25(2):315–22.
- [113] Garcia-Aparicio MP, Ballesteros M, Manzanares P, Ballesteros I, Gonzalez A, Negro MJ. Xylanase contribution to the efficiency of cellulose enzymatic hydrolysis of barley straw. Applied Biochemistry and Biotechnology 2007;136–140:353–65.
- [114] Kumar R, Wyman CE. Effects of cellulase and xylanase enzymes on the deconstruction of solids from pre-treatment of poplar by leading technologies. Biotechnology Progress 2009;25:302–14.
- [115] Beukes N, Pletschke Bl. Effect of alkaline pre-treatment on enzyme synergy for efficient hemicellulose hydrolysis in sugarcane bagasse. Bioresource Technology 2011;102:5207–13.
- [116] Olver B, Van Dyk JS, Beukes N, Pletschke BI. Synergy between EngE, XynA and ManA from Clostridium cellulovorans on corn stalk, grass and pineapple pulp substrates. 3. Biotechnology 2011:1(4):187–92.
- [117] Zykwinska AW, Ralet M-CJ, Garnier CD, Thibault J-FJ. Evidence for in vitro binding of pectin side chains to cellulose. Plant Physiology 2005;139:397–407.
- [118] Caffall KH, Mohnen D. The structure, function, and biosynthesis of plant cell wall pectic polysaccharides. Carbohydrate Research 2009;344:1879–900.
- [119] Lima DU, Loh W, Buckeridge MS. Xyloglucan-cellulose interaction depends on the sidechains and molecular weight of xyloglucan. Plant Physiology and Biochemistry 2004;42:389–94.
- [120] Zykwinska A, Thibault J-F, Ralet M-C. Organization of pectic arabinan and galactan side chains in association with cellulose microfibrils in primary cell walls and related models envisaged. Journal of Experimental Botany 2007:1–8
- [121] Coimbra MA, Rigby NM, Selvendran RR, Waldron KW. Investigation of the occurrence of xylan-xyloglucan complexes in the cell walls of olive pulp. Carbohydrate Polymers 1995;27:277–84.
- [122] Thompson JE, Fry SC. Evidence for covalent linkage between xyloglucan and acidic pectins in suspension-cultures rose cells. Planta 2000;211:275–86.
- [123] Arnous A, Meyer AS. Discriminated release of phenolic substances from red wine grape skins (*Vitis vinifera L.*) by multicomponent enzymes treatment. Biochemical Engineering Journal 2010;49:68–77.
- [124] Capek P, Renard CM, Thibault J-F. Enzymatic degradation of cell walls of apples and characterization of solubilized products. International Journal of Biological Macromolecules 1995;17(6):337–40.
- [125] Pakarinen A, Zhang J, Brock T, Maijila P, Viikari L. Enzymatic accessibility of fiber hemp is enhanced by enzymatic or chemical removal of pectin. Bioresource Technology 2012;107:275–81.
- [126] Kuhad RC, Gupta R, Khasa YP, Singh A, Zhang Y-HP. Bioethanol production from pentose sugars: current status and future prospects. Renewable and Sustainable Energy Reviews 2011;15:4950–62.
- [127] Grohmann K, Baldwin EA. Fermentation of galacturonic acid and other sugars in orange peel hydrolysates by the ethanologenic strain of *Eschericia coli*. Biotechnology Letters 1994;16(3):281–6.
- [128] Grohmann K, Cameron RG, Buslig BS. Fermentation of sugars in orange peel hydrolysates to ethanol by recombinant Eschericia coli KO11. Applied Biochemistry and Biotechnology 1995;51–52:423–35.
- [129] Grohmann K, Manthey JA, Cameron RG, Buslig BS. Fermentation of galacturonic acid and pectin-rich materials to ethanol by genetically modified strains of *Erwinia*. Biotechnology Letters 1998;20(2):195–200.